Differential Capacity of the Double-Layer Formed at a Solid Electrode (Pt, Au)/Ionic Liquid Interface

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The differential capacity at the electrode (Pt, Au)/ionic liquid interface of 18 ionic liquids (ILs), was measured applying chronoamperometry. The measurements were done by a two electrode system. The double layer capacity at the Pt/IL and Au/IL interface was 1 – 8 μF/cm^2. The capacity, estimated from the impedance measurements, was approximately constant within a potential range of ca. 3 V.

Key words: Double-Layer Capacity; Ionic Liquids.

1. Introduction

Salts of low melting points, usually called ionic liquids (ILs), have been studied extensively during the last decade [1 – 3]. These liquid salts may serve as solvents for chemical reactions as well as electrolytes in electrochemical devices. The first extensively studied IL was 1-ethyl-3-methyl-imidazolium tetrachloroaluminate ([EMIm][AlCl$_4$]). However such ionic liquids containing AlCl$_4$$^-$ are easily hydrolyzed by water. Non-chloroaluminate ILs, more resistive to moisture, have been developed recently. At the same time electrochemical double-layer capacitors (EDLCs), based on carbon materials having a very high surface area, have been developed with very promising results. Both aqueous and non-aqueous liquid electrolytes, as well as solid polymer electrolytes, have been applied [4 – 16]. There are also very promising attempts to apply ionic liquids in EDLCs [17 – 25]. The papers mentioned above report the capacity of devices prepared of different types of activated carbons (AC). The specific capacity of the AC/electrolyte interface has usually been expressed versus the carbon total mass (in F/g) or versus the total carbon surface estimated from the BET isotherm (in μF/cm^2). There are only a few publications about the double-layer capacity measured at a geometrically defined electrode/electrolyte surface. Apart from the report on ionic liquids based on the chloroaluminate ion [26], a paper on the specific capacitance for glassy carbon (GC), mercury and a commercial carbon as electrode materials and four ionic liquids based on the 1-ethyl-3-methyl-imidazolium cation can be found in the literature [27]. The general aim of this work was to examine the different capacity at the solid electrode/IL interface for a number of ionic liquids and well-defined metal electrodes: Pt and Au.

2. Experimental

2.1. Chemicals

Bromoethane (Merck, for synthesis), 1-bromopropane (Merck, for synthesis), chloroform (P.O.Ch., Poland, p.p.a.) and tetrahydrofuran (Merck, for synthesis) were distilled prior to their use. An aqueous solution of silver tetrafluoroborate (AgBF$_4$) was prepared by reacting tetrafluoroboric acid (HBF$_4$, Fluka, 48% solution in water) with silver oxide (P.O.Ch.). The ionic liquids 1-butyl-4-methyl-pyridinium tetrafluoroborate [BMPi][BF$_4$] and 1-ethyl-3-methyl-imidazolium trifluoromethanesulfonate [EMIm][OTf] were purchased from Sigma-Aldrich. The ionic liquids 1-ethyl-3-methyl-imidazolium tetrafluoroborate [EMIm][BF$_4$], 1-ethyl-3-methyl-imidazolium bis(trifluoromethyl)imide [EMIm][NTf$_2$], 1-butyl-3-methyl-imidazolium tetrafluoroborate [BMIm][BF$_4$], 1-butyl-3-methyl-pyrrolidinium bis(trifluoromethyl)-imide [BMPy][NTf$_2$], and 1-methyl-3-propyl-pyrrolidinium bis(trifluoromethyl)imide [MPPy][NTf$_2$] were prepared according to published proce-

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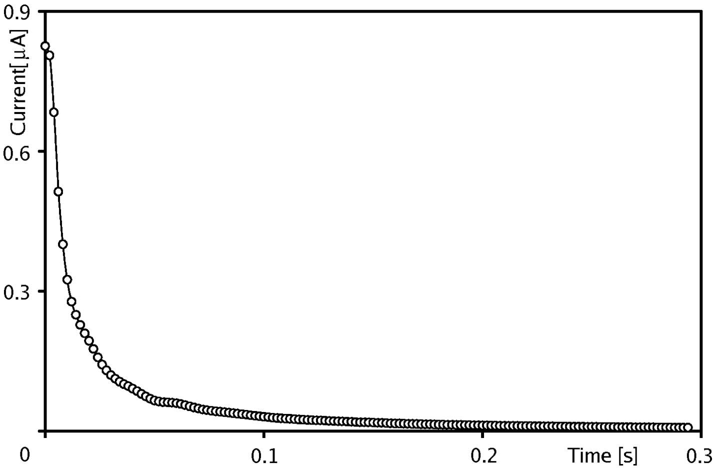

Fig. 1. Current response to a potential distortion of −90 mV. Ionic liquid: [EMIm][OTf]; working electrode: platinum wire with a diameter of 1.6 mm. $T = 298$ K.

dures [23]. 1-Ethyl-3-methyl-imidazolium bromide [EMIm][Br] and 1-butyl-3-methyl-imidazolium bromide [BMIm][Br] were prepared by the substitution of bromoethane or bromobutane 1-methylimidazole (Fluka) in chloroform. 1-Ethyl-3-methyl-imidazolium tetrafluoroborate [EMIm][BF_4] was obtained by titration of an aqueous solution of $AgBF_4$ with an aqueous solution of [EMIm][Br] versus a silver indicating electrode [23]. [EMIm][BF_4] was checked for residual bromide using aqueous $AgNO_3$ (no AgBr precipitate was detected). 1-Methyl-3-propyl-imidazolium bromide [MPIm][Br] was obtained by substitution of 1-bromopropane with 1-methylimidazole in tetrahydrofuran [28]. Dialkylimidazolium bromides were purified by washing with *n*-hexane. The ionic liquids 1-pentoxymethyl-imidazolium tetrafluoroborate [C_5OmIm][BF_4], 1-butoxymethyl-imidazolium L-lactate [C_4OmIm][Lact(L)], 1-butoxymethyl-imidazolium lactate [C_4OmIm][Lact(DL)], 1-methyl-3-*H*-imidazolium lactates (L and DL) [MHIm][Lact(DL)] and [MHIm][Lact(L)], as well as ethoxymethyl(2-hydroxyethyl) dimethylammonium bis(trifluoromethyl)imide [(C_2Om)DAE][NTf_2] were obtained from the J. Pernak group (Poznan University of Technology) [29, 30]. The water content, analyzed with a Karl Fischer titrant (Aldrich), was below the detection limit.

2.2. Measurements

The differential capacity at the electrode/IL interface was measured chronopotentiometrically by a two electrode system. The working electrode was placed in a glass cell with thermostating water-jacket, filled with the ionic liquid. A platinum foil with a surface of ca. 2 cm^2 served as auxiliary electrode. The working Pt (radius 1.68 mm, surface of 0.0222 cm^2) and Au (radius 1.60 mm, surface of 0.02011 cm^2) electrodes were from Mineral (Poland). In the two electrode measurements the high surface (ca. 2 cm^2) Pt or Au foils served both as auxiliary and pseudo-reference electrodes. The working Pt or Au electrode was charged by superimposing a ±10, 20, 30, 50 up to 90 mV potential dc signal (U) over ca. 100 ms. The current flowing during the charging and discharging of the electrode was recorded as a function of time. The charge Q accumulated at the electrode was obtained by integrating the $I = f(t)$ curves.

3. Results and Discussion

Figure 1 shows an example of an experimental chronoamperometric curve: the current response to the distortion of the open circuit potential, recorded versus time. The current vs. time curve decays monotonically to the baseline, indicating a pure capacitive behaviour of the electrode/electrolyte interface, with no Faradayic processes. The integration of the curve ($Q = It$) gave a charge of 15.8 nC. Figure 2 shows the charge necessary for loading the double layer at different potential signals (in a range from −90 mV to +90 mV). The slope of the straight line indicates directly the differential capacity of the electrode/IL interface double-layer: $C = \mathrm{d}Q/\mathrm{d}U$. The double-layer capacities, collected in Table 1 (for both Pt/IL and Au/IL interfaces) were determined at a level typically between a few μF/cm^2 and 8 μF/cm^2. These values are somewhat lower or comparable to those reported for the

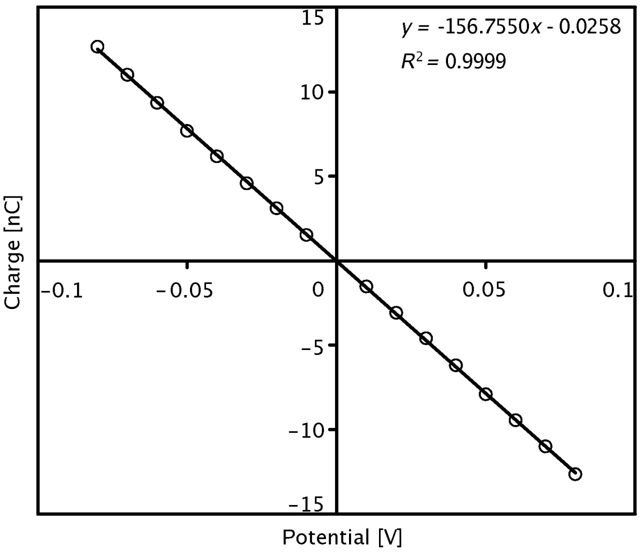

Fig. 2. Dependence of the charge accumulated on the electrode after applying a potential distortion of different amplitude. Ionic liquid: [EMIm][NTf_2]; working electrode: platinum wire with a diameter of 1.6 mm. $T = 298$ K.

Table 1. Differential double-layer capacity of the solid electrode/ionic liquid interface.

Ionic liquid		C_{dl} [μF/cm^2]	
		Pt	Au
[BMIm]$^+$	[BF_4]$^-$	1.4	3.1
[BMIm]$^+$	[NTf_2]$^-$	1.2	2.5
[MPPy]$^+$	[NTf_2]$^-$	0.9	1.2
[EMIm]$^+$	[NTf_2]$^-$	7.2	3.2
[EMIm]$^+$	[BF_4]$^-$	3.4	6.8
[BMPy]$^+$	[NTf_2]$^-$	1.5	5.0
[BMIm]$^+$	[Br]$^-$	5.1	2.5
[C_5OmIm]$^+$	[BF_4]$^-$	3.9	4.0
[MPIm]$^+$	[Br]$^-$	5.3	3.2
[EMIm]$^+$	[OTf]$^-$	2.9	1.7
[C_4OmIm]$^+$	[Lact(L)]$^-$	4.2	2.8
[C_4OmIm]$^+$	[Lact(DL)]$^-$	3.6	2.3
[MHIm]$^+$	[Lact(L)]$^-$	3.9	4.5
[MHIm]$^+$	[Lact(DL)]$^-$	4.4	4.4
[BMPi]$^+$	[BF_4]$^-$	8.1	3.5
[(C_2Om)DAE]$^+$	[NTf_2]$^-$	7.0	3.1
[(C_2Om)DecDAE]$^+$	[NTf_2]$^-$	4.5	4.1
[(C_2Om)AcDAE]$^+$	[Ace]$^-$	7.3	5.7

Hg/BuPyrCl·$AlCl_3$ [26] and GC/[EMIm][NTf_2] interfaces [27]. Carbon materials, including activated carbons and glassy carbon, are popular electrode materials in spite of the fact that they are in general chemically and electrochemically unstable [31–33]. Even in contact with atmospheric oxygen the carbon surface is readily oxidized with formation of such functionalities as carboxy, hydroxy or carbonyl groups. The oxygen to carbon ratio may be as high as 0.2 [32]. These functionalities are electrochemically active and therefore may undergo Faradayic redox reactions. In addition, the carbon material may possess cracks or pores and, hence, a higher effective surface than the geometric surface. All this may lead to an erroneous interpretation of the chronoamperometric experiments. High surface activated carbons, as relatively inexpensive materials, are employed as electrodes in most electrochemical capacitors available today. Probably the significant part of the device capacity is of pseudocapacitive (Faradayic) nature. Moreover, both activated carbons, as well as glassy carbons, may be produced from different precursors and under different conditions, which results in a variety of final products. Most of the work on the specific capacity of the interface formed between metals and inorganic melts was done in the sixties and seventies of the XX-th century, with the result that they point to the minimum differential capacity of ca. 10–20 µF/cm^2. However, recently the double-layer capacity of the Pb/NaCl-KCl melt was re-measured with the impedance technique in the frequency range of 10 Hz to 500 kHz. The C_{dl} was separated, assuming that the equivalent circuit contained inductance [34]. The result of the procedure (measurements and impedance fitting) led to a C_{dl} at a level below 1 µF/cm^2.

Although the process of the double-layer charging takes place at a two-dimensional electrode/electrolyte interface, practical EDLC devices consist of a three-dimensional carbon electrode of different pore distribution. In the case of activated carbons of a very high specific surface a significant volume of the material is not accessible for the electrolyte (micropores) [12]. Therefore, the calculation of the specific capacitance (expressed in μF/cm^2) of the active surface may be misleading. Such calculations indicate that the specific capacitance related to the BET surface is usually between 5 and 10 μF/cm^2. In the case of the [EMIm][NTf$_2$] electrolyte the capacitance was 11.7 μF/cm^2 at the dropping mercury electrode and 12.0 μF/cm^2 at GC, but only 3.7 μF/cm^2 at a high surface SpectraCarb 2220 yarn (ca. 2000 m^2/g BET specific surface, but with unknown active carbon/electrolyte surface) [27]. On the other hand, the values listed in Table 1 were obtained at well-defined metal/electrolyte interfaces.

4. Conclusions

The double layer capacity at a well-defined metal/IL interface (Pt/IL or Au/IL), obtained by chronoamperometry, is at the level of $1-8$ μF/cm^2 at potentials close to the open circuit potential.

Acknowledgements

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